Supplementary Information

Design and coupling of multifunctional TiO$_2$ nanotube photonic crystal to nanocrystalline titania layer as semi-transparent photoanode for dye-sensitized solar cell

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Simulation and theoretical calculations:

For the theoretical calculations, the light harvesting efficiency (LHE) is defined as the fraction of light intensity absorbed by the dye at a certain wavelength in the DSSC\textsuperscript{1, 2}:

\[
LHE = \frac{A}{I_0} = \frac{I_\lambda}{I_0}
\] (1)

where \( A \) is absorptance, \( I_\lambda \) is the absorbed intensity and \( I_0 \) is the incident one. IPCE is defined as the number of generated electrons divided by the number of incident photons, which is proportional to LHE or absorptance, and given by the following equation\textsuperscript{3}:

\[
\text{IPCE} = (LHE)\phi\eta = A\phi\eta
\] (2)

where \( \phi \) is the quantum yield of charge injection, and \( \eta \) is the charge-collection efficiency by the photoanode. The generated \( J_{sc} \) can be calculated by the expression\textsuperscript{3}:

\[
J_{sc} = \int q\text{IPCE}(\lambda)F(\lambda)d\lambda = \int qLHE(\lambda)\phi(\lambda)\eta(\lambda)F(\lambda)d\lambda
\] (3)

where \( q \) is the electron charge, and \( F(\lambda) \) is the incident photon flux, which is calculated from the standard AM1.5 solar spectral irradiance\textsuperscript{4}. Since, in our study, \( \phi(\lambda) \) and \( \eta(\lambda) \) are weakly dependent of the wavelength \( \lambda \), equation (3) can be simplified to the following form:

\[
J_{sc} = \int qLHE(\lambda)F(\lambda)d\lambda = \int qA(\lambda)F(\lambda)d\lambda
\] (4)

By comparing the absorptance of the TiO\textsubscript{2} NT PC based DSSC (LHE\textsubscript{pc}) to that of the standard DSSC (LHE\textsubscript{standard}), the enhancement of the photocurrent efficiency \( \frac{\Delta J_{sc}}{J_{sc}} \) can be estimated according to the following expression\textsuperscript{2}:

\[
\frac{\Delta J_{sc}}{J_{sc}} = \frac{\int LHE_{pc}(\lambda)F(\lambda)d\lambda - \int LHE_{standard}(\lambda)F(\lambda)d\lambda}{\int LHE_{standard}(\lambda)F(\lambda)d\lambda}
\] (5)
**Fig. S1** Photographs of the TiO$_2$ NT PC samples with different HC pulse durations of 20, 30, 40 and 50s, from left to right, respectively.

**Fig. S2** Experimental and simulated reflectance spectra under near normal incidence on the photoanodes with lattice constants of 120, 150, 190 and 230 nm (120-PC/TiO$_2$ NP, 150-PC/TiO$_2$ NP, 190-PC/TiO$_2$ NP, and 230-PC/TiO$_2$ NP, respectively) in ethanol. The background reflectance from the FTO-coated glass substrate covered with TiO$_2$ NP was subtracted.
As seen from Fig. S3, the thickness of the TiO$_2$ NP absorbing layer and TiO$_2$ NT PC is about 10 and 2.3 μm, respectively, for the TiO$_2$ NT PC/TiO$_2$ NP photoanode (Fig. S3a and d). The thickness of TiO$_2$ NT/TiO$_2$ NP photoanode (Fig. S3b and e) is the same as that of the TiO$_2$ NT PC/TiO$_2$ NP one, while that of the TiO$_2$ NP layer is about 12 μm in the reference cell (Fig. S3c and f).

**Fig. S3** (a) FESEM top view and (d) cross-section images of the TiO$_2$ NT PC/TiO$_2$ NP photoanode; (b) FESEM top view and (e) cross-section images of the TiO$_2$ NT /TiO$_2$ NP photoanode; (c) FESEM top view and (f) cross-section image of the TiO$_2$ NP photoanode.
Figure S4 shows the Bode phase plot of the electrochemical impedance spectroscopy (EIS) of different photoanodes. The electron lifetime ($\tau_r$) was calculated from the plot shown in Fig. S4 by $\tau_r=1/(2\pi f_{\text{peak}})$, where $f_{\text{peak}}$ is the frequency where the characteristic peak locates in the mid-frequency (1-100 Hz) range. It can be found that the electron lifetimes for all the photoanodes with TiO$_2$ nanotubes (no matter with or without the PC structure) are quite similar, ranging from 12.7~13.7 ms. This is slightly higher than that of the photoanode without nanotubes (TiO$_2$ NP), which is around 10.7 ms. Such an increase in the life time may contribute to the slight increase in $V_{oc}$ from 0.68 eV (for photoanodes without nanotubes) to 0.69~0.70 eV (for photoanodes with nanotubes), but is insufficient to contribute significantly to the power conversion efficiency enhancement observed in our samples. For comparison, a 10-fold change in recombination rate generally results in a change of 0.05 eV in $V_{oc}$ and a 2-fold change only shifts the $V_{oc}$ by 0.02-0.03 eV. The insignificant increase of electron lifetime in photoanodes (with TiO$_2$ nanotubes) can be attributed to the limited thickness of the nanotube layer used (as compared to the thickness of the nanoparticle layer).

![Bode phase plots of different photoanodes measured with an alternating-current amplitude of 10 mV under the AM1.5 illumination.](image)
It can be seen from Fig. S5 that, within the photonic bandgap range, the PC acts as a Bragg mirror to reflect photons back, which causes strong photon resonance modes in the absorbing layer. For the frequency at the red edge of the bandgap, the field maxima are located at the parts of higher refractive index (dye-sensitized TiO$_2$), which may also result in a higher red light absorption near the low-frequency edge of the bandgap. Meanwhile, at the high-frequency edge, the field maxima are shifted to the parts of lower refractive index (electrolyte).

![Fig. S5](image)

**Fig. S5** (a) Simulated reflectance spectrum of NT PC (with lattice constants of 150nm) in electrolyte. (b-d) Distribution of the amplitude square of the electric field in different parts of the photoanode at three selected wavelengths shown in (a): (b) $\lambda_2$, within the bandgap, (c) $\lambda_3$, at the red edge and (d) $\lambda_1$, at the blue edge of the bandgap. For comparison, the distribution of the amplitude square of the electric field in a standard DSSC is also plotted (dotted line).
References:


